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16. ABSTRACT

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EVALUATION OF NUMERICAL SCHEMES FOR SOLVING A CONSERVATION OF SPECIES EQUATION WITH CHEMICAL TERMS

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Abstract—Numerical methods are investigated for solving a system of continuity equations that contain linear and nonlinear chemistry as source and sink terms. It is shown that implicit, finite-difference approximations, when applied to the chemical kinetic terms, yield accurate results when the equations are linear, but give poor results when the equations are nonlinear. In fact, when the equations are nonlinear, the implicit finite-difference scheme will be unstable if Δt is large. It is shown that for urban and larger scale air quality simulation models, the advection and chemical terms can be handled separately for each time step. This technique yields results that are more accurate than implicit treatments of the chemistry.

1. INTRODUCTION

Accurate and efficient numerical procedures for solving the partial differential equations describing the transport, diffusion and transformation processes occurring in polluted atmospheres are of major importance to the development of air quality simulation models.

Though a great deal of work has been reported in the literature (see for example: Bryan, 1966; Fromm, 1968; Grammeltvedt, 1969; Long and Pepper, 1976) concerning the problems of solving the advection terms of the equations of motion and continuity equations, and many papers (see for example: Gupta, 1976; Seinfeld *et al.*, 1970) on the solution of stiff ordinary differential equations, there is a scarcity of results concerning techniques for solving continuity equations with complex source and sink terms, specifically linear and nonlinear chemical reactions. The only technique that has been used and reported in the meteorological and air pollution literature is that of Reynolds *et al.* (1973), where implicit methods were used.

As will be shown in this paper, implicit techniques are accurate for linear chemistry but can be very inaccurate when used with nonlinear systems. Seemingly, one's only choice is to use explicit methods to solve the chemistry and advection (diffusion will not be considered in this paper). This can be very expensive if either the chemistry or advection approximations require small time steps for stability. Typical urban and regional scale air quality simulation grid point models generally allow advection time steps of the order of 2–4 min for 1 km grid spacing to as much as 30 min time steps for 80 km grid spacings. The chemical kinetic terms will generally require time steps of the order of seconds. This disparity in time scales for these two processes suggests that the separation and independent solution of the chemical kinetic portions of the conservation of mass equation for any one advection time step would be advantageous.

This paper examines through numerical experiments the feasibility of separating the solutions of the advective and chemical kinetic portions of the partial differential equations and evaluates the relative efficiency and errors associated with this solution method.

The advection and reaction kinetics of two chemical systems are examined by numerical experimentation in one dimensional models. The first chemical kinetic system

$$A \xrightarrow{k_1} B, \tag{1}$$

$$B \xrightarrow{k_2} A, \tag{2}$$

$$B \xrightarrow{k_3} C, \tag{3}$$

yields the following linear, partial differential equations

$$\frac{\partial A}{\partial t} + \nabla \cdot A\mathbf{V} = -k_1 A + k_2 B, \tag{4}$$

$$\frac{\partial B}{\partial t} + \nabla \cdot B\mathbf{V} = k_1 A - (k_2 + k_3)B, \tag{5}$$

$$\frac{\partial C}{\partial t} + \nabla \cdot C\mathbf{V} = k_3 B, \tag{6}$$

where t is time, Δ is the three-dimensional divergence operator, $\mathbf{V}$ is the three-dimensional, time-averaged velocity (assumed constant in this paper) and k_1, k_2

* On assignment from the National Oceanic and Atmospheric Administration, U.S. Department of Commerce.

k_3 are chemical reaction rate constants. The second chemical system considered is

$$A \xrightarrow{k_1} B + C, \tag{7}$$

$$B + C \xrightarrow{k_2} A, \tag{8}$$

$$C + 2A \xrightarrow{k_3} 2D, \tag{9}$$

which yields the following nonlinear system of partial differential equations:

$$\frac{\partial A}{\partial t} + \nabla \cdot A\mathbf{V} = -k_1 A + k_2 BC - 2k_3 CA^2, \tag{10}$$

$$\frac{\partial B}{\partial t} + \nabla \cdot B\mathbf{V} = k_1 A - k_2 BC, \tag{11}$$

$$\frac{\partial C}{\partial t} + \nabla \cdot C\mathbf{V} = k_1 A - k_2 BC - k_3 CA^2, \tag{12}$$

$$\frac{\partial D}{\partial t} + \nabla \cdot D\mathbf{V} = 2k_3 CA^2. \tag{13}$$

It should be noted that the A^2 term in (10) makes this equation nonlinear and therefore standard analysis techniques cannot be applied to this system of equations. As is commonly done, we have assumed that techniques that do not work well for linear systems will not work well for nonlinear systems.

In section II, it is shown by an elementary stability analysis that forward-in-time differencing is preferable to central-time differencing. This same analysis indicates that based on stability only, implicit handling of the chemistry is preferable to explicit techniques. Also in this section a modified explicit technique is developed which is shown in section III to be more accurate than the implicit scheme for the nonlinear chemical system.

II. NUMERICAL PROCEDURE

In order to evaluate time-difference stability criteria of the chemical kinetic portions of the partial differential equations, a finite Fourier series analysis (von Neumann; see Roache, 1972) was performed on equations (14) and (15) below

$$\frac{\partial A}{\partial t} = -k_1 A, \tag{14}$$

$$\frac{\partial A}{\partial t} = +k_1 A. \tag{15}$$

Physically only (14) is reasonable but (15) can result if negative concentrations are generated by either advection or time-differencing errors and therefore a stability analysis must consider both (14) and (15).

The results, shown in Table 1, indicate (14) and (15) are unstable for explicit, central-in-time schemes (Methods 1 and 5); the explicit, forward-in-time approximation to (14) (Method 2) is stable if the solution is always positive, but for negative A Method 2 becomes Method 6 which is unconditionally unstable. The implicit approximations to (14) and (15) (Methods 3, 4, 7 and 8) are unconditionally stable and positive for $\Delta t \geq 2/k_1$.

There are three candidates for the time differencing: explicit and forward-in-time (Method 2), implicit and forward-in-time (Method 3), and implicit and central-in-time (Method 4).

The explicit, forward-in-time method (Method 2) requires that the concentrations be positive or it is unstable. This restriction of positive values is very demanding because standard advection schemes will generate negative values in the vicinity of large gradients.

The central-in-time scheme is undesirable because it requires the storage of three time levels. In urban scale air pollution models, the large number of species equations required for a reasonable simulation will tax most computer systems even if two time levels are used. Therefore, this paper will only consider the use of forward time differencing.

In summary forward time differencing with implicit chemistry (Method 3) is stable for both positive and negative concentrations and appears to be the best choice since the forward-in-time, explicit chemistry scheme (Method 2) becomes unstable if negative concentrations are generated. Central-in-time schemes are not considered since they require 50% more computer core storage than forward-in-time schemes.

The technique that is proposed is forward-in-time and explicit with respect to the chemistry. To see how the technique works, consider the one-dimensional (in space) continuity equation.

$$\frac{\partial A}{\partial t} + \frac{\partial uA}{\partial x} = -k_1 A. \tag{16}$$

The method of fractional steps (Yanenko, 1971) suggests the possibility of treating (16) in two parts; the first, an advection calculation with time step $\Delta t_{adv} = \Delta x/u$, and the second, a chemical calculation with each time step restricted to $\Delta t_{chm} \leq 1/k_1$. The

Table 1. A summary of stability criteria for various numerical methods for solving the equations, $\partial A/\partial t = -k_1 A$ and $\partial A/\partial t = +k_1 A$

Method	Stability
$\partial A/\partial t = -k_1 A$	
1. $A_j^{n+1} - A_j^{n-1} = -2\Delta t k_1 A_j^n$	Unstable for all $\Delta t \geq 0$
2. $A_j^{n+1} - A_j^n = -\Delta t k_1 A_j^n$	Stable for $0 \leq \Delta t \leq 2/k_1$ positive for $\Delta t \leq 1/k_1$
3. $A_j^{n+1} - A_j^n = -\Delta t k_1 A_j^{n+1}$	Stable for all $\Delta t \geq 0$ positive for all $\Delta t \geq 0$
4. $A_j^{n+1} - A_j^{n-1} = -2\Delta t k_1 A_j^{n+1}$	Stable for all $\Delta t \geq 0$ positive for all $\Delta t \geq 0$
$\partial A/\partial t = +k_1 A$	
5. $A_j^{n+1} - A_j^{n-1} = 2\Delta t k_1 A_j^n$	Unstable for all $\Delta t \geq 0$
6. $A_j^{n+1} - A_j^n = \Delta t k_1 A_j^n$	Unstable for all $\Delta t \geq 0$
7. $A_j^{n+1} - A_j^n = \Delta t k_1 A_j^{n+1}$	Stable for all $\Delta t \geq 2/k_1$ positive $\Delta t < 1/k_1$
8. $A_j^{n+1} - A_j^{n-1} = 2\Delta t k_1 A_j^{n+1}$	Stable for $\Delta t \geq 1/k_1$

chemistry is performed until the chemical time equals the advection time. The advection calculation is carried out using van Leer's (1974) modified zero average phase error method, which is conservative and will not produce negative concentrations as long as u does not change sign. The technique of splitting the chemical calculations from the advection calculations has been used by Rizzi and Bailey (1976), and Eskridge and Demerjian (1976). Rizzi and Bailey have used an explicit technique to solve the advection portion of the equations and an implicit scheme to solve the chemical portion of a linear set of conservation of species equations.

While in this paper the chemistry in the modified explicit scheme is solved using explicit finite difference methods, this does not mean that other methods such as Gear (1971) cannot be used instead and, in fact, may be preferable.

To summarize, first solve

$$\frac{\partial A}{\partial t} + \frac{\partial uA}{\partial x} = 0, \tag{17}$$

by use of van Leer's method for time step $(\Delta t)_{adv}$ which is forward-in-time. Then,

$$\frac{\partial A}{\partial t} = -k_1 A, \tag{18}$$

is solved by use of forward-in-time differences and explicit chemistry, with step size $\Delta\tau_{chm}$, until the chemistry time agrees with the advection time.

The process of first calculating advection and then chemistry is repeated as long as desired.

III. RESULTS

In this section, we shall present the results of several one-dimensional (in space) computer experiments which show that for the linear system, (1)–(6), the implicit scheme is to be preferred to the modified explicit. However, for the nonlinear system, (7)–(13) the modified explicit method gives more accurate results than the implicit even though it is slower.

In order to provide a severe test for the numerical schemes used in solving the advective and chemical kinetic systems, a square wave with relatively "stiff" chemical reaction sets were considered for the experimental model systems. For the square wave problem in one-dimension with constant velocity, van Leer's advection scheme will reproduce the square wave exactly if the maximum allowable time step ($\Delta t_{max} = \Delta x/u$) is used. Therefore, two cases were used; first with $\Delta t_{adv} = 0.9\Delta t_{max}$ (Δt_{adv} is the advection time) and $\Delta t_{adv} = 0.5\Delta t_{max}$, this resulted in a small amount of numerical diffusion in the first case and a larger amount for the latter case.

The purpose in doing the two test cases is that many numerical schemes have a truncation error which is a function of the time step as is van Leer's scheme. This means the error in the calculations is not constant across a grid and, as the following analysis shows, the error is different for the different components. It should be noted that if there is no diffusion the solutions to (4)–(6) and (10)–(13) should match the Gear solutions. This is found to be true (results not presented) for the linear system for the implicit and modfied explicit schemes. However, for the non-linear system, it was found that the implicit scheme does not agree with the Gear solutions and the modified explicit does agree with the Gear solutions.

It should be noted that in the case of a constant wind and initial square wave distributions of A, B, C or D that the left side of equations (4)–(6) and (10)–(13) can be written as total derivatives, d/dt. This means, of course, that they can be solved as ordinary differential equations and hence solutions are available to compare results with computer experiments. The analytic solution to the chemical system (4)–(6) reported by Aberty and Miller (1957) was compared with results generated from the Gear (1971) numerical integration technique for "stiff" ordinary differential equations. The purpose here was to establish the overall accuracy of this technique so that comparisons could be made with the Gear results for the second chemical system (10)–(13), since an analytical solution to this reaction set does not exist. As shown in Fig. 1, the Gear results are quite accurate. (The Gear routine calculation used an $\epsilon = 10^{-4}$ and the Jacobian was solved by Gaussian elimination.)

The numerical experiments were performed in one-spatial dimension with a grid spacing of 1.25 km, a grid of 16 points ($x_i = i\ \Delta x$, $i = 1, \ldots, 16$) and cyclic boundary conditions.

A constant velocity of 5 m s^{-1} is used in all experiments which yields a maximum advection time step, Δt_{max}, of 250 s.

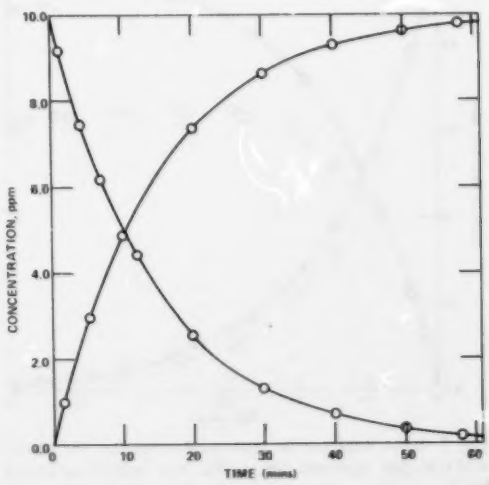

Fig. 1. Solid lines are the analytical solutions and circles represent the Gear solutions for the A and C components.

The initial conditions (19) define the square wave used in the chemical system (4)–(6).

$$A = \begin{cases} 10\text{ ppm } x_i;\ i = 3,4,5 \\ 0 \quad \text{otherwise} \end{cases}$$
$$B = C = 0\text{ ppm } i = 1,\ldots,16. \tag{19}$$

The chemical reaction rate constants

$$k_1 = 0.2\,\text{min}^{-1},\ k_2 = 100\,\text{min}^{-1},\ k_3 = 50\,\text{min}^{-1}, \tag{20}$$

were chosen such that the system is "relatively stiff". The intent is to require time steps for the chemical integration process to be significantly smaller than time steps required in the advection calculation. This set of reaction constants yields $\Delta t_{\text{chm}} = 0.6$ s.

Figure 2 shows the results of two simulations for the A and C components. The experiments shown in Fig. 2 are the modified explicit and implicit techniques for the cases of $\Delta t = 0.9\Delta t_{\max}$ and $\Delta t = 0.5\Delta t_{\max}$. The values plotted in Fig. 2 and all other figures represent the maximum value of the pollutant species at that time.

Figure 2 shows that the explicit and implicit scheme give almost exactly the same results and, since the implicit scheme requires fewer calculations, it is to be preferred for linear systems.

The nonlinear chemistry experiments were performed in a similar manner to the linear case; using the same grid system and boundary conditions. The initial conditions used were

$$A = \begin{cases} 1\text{ ppm } x_i;\ i = 3,4,5 \\ 0 \quad \text{otherwise} \end{cases} \tag{21}$$
$$B = \begin{cases} 0.1\text{ ppm if } i = 3,4,5 \\ 0 \quad \text{otherwise} \end{cases}$$
$$C = \begin{cases} 0.16\text{ ppm, if } i = 3,4,5 \\ 0 \quad \text{otherwise} \end{cases}$$

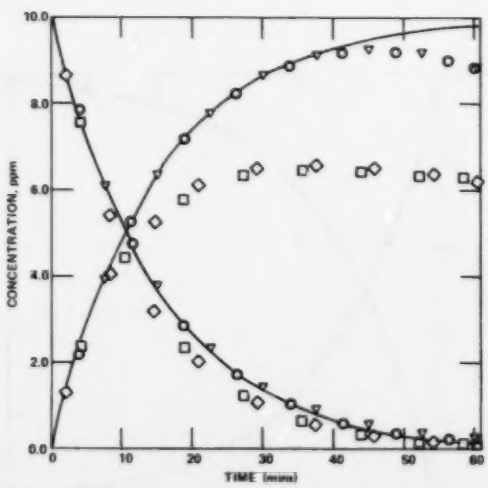

Fig. 2. Solid lines are the analytical solutions, the circles and triangles represent the explicit and implicit solutions for $\Delta t_{\text{adv}} = \Delta t_{\max}$, respectively; the box and diamond represent the explicit and implicit solutions for $\Delta t_{\text{adv}} = 0.5\ \Delta t_{\max}$, respectively.

with chemical reaction rate constants

$$k_1 = 0.4\,\text{min}^{-1},$$
$$k_2 = 25\,\text{min}^{-1},$$
$$k_3 = 0.1\,\text{min}^{-1}. \tag{22}$$

The finite-difference equation used for the reactive part of (10) in the implicit scheme is shown below since it is the only nonstandard approximation

$$\frac{A_j^{n+1} - A_j^n}{\Delta t} = -k_1 A_j^{n+1} + k_2 B_j^n C_j^n - 2k_3 C_j^n A_j^n A_j^{n+1}. \tag{23}$$

Equation (10) can also be approximated by

$$\frac{A_j^{n+1} - A_j^n}{\Delta t} = k_1 A_j^{n+1} + k_2 B_j^n C_j^n - 2k_3 C_j^n (A_j^{n+1})^2, \tag{24}$$

but preliminary results (not shown) indicate that this scheme is very inaccurate.

In Fig. 3. the results of several implicit calculations and the modified explicit method for the A component are shown. The explicit results are very accurate while the implicit results are not as good. In fact, the implicit calculations show that $\Delta t_{\text{chm}} = \Delta t_{\text{adv}}$ is unstable which is surprising since standard implicit schemes are stable for all $\Delta t > 0$.

Experimentally, we have found that the best implicit results are obtained with a chemical time step one half of the advective time step.

Figure 4 shows the results for the large numerical diffusion case for the A component. This is the only figure that seems to indicate that the implicit scheme is superior to the modified explicit scheme. However, this can be misleading, since the implicit scheme first

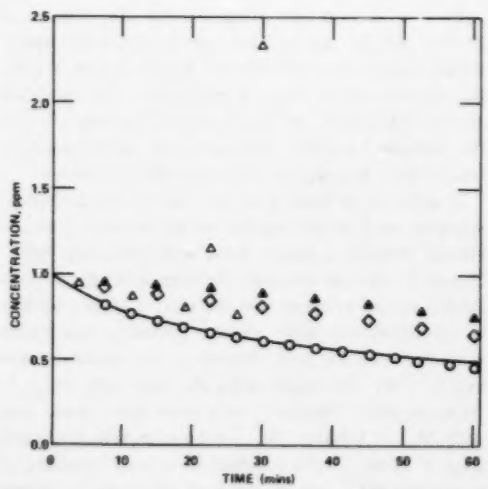

Fig. 3. Solid line is the Gear solution of the A component, the circles are the modified explicit solutions, the open triangles are the implicit solutions for $\Delta t_{\text{chm}} = \Delta t_{\text{adv}}$, the solid triangles are the implicit solutions for $\Delta t_{\text{chm}} = 0.25\ \Delta t_{\text{adv}}$, the diamonds are the implicit solutions for $\Delta t_{\text{chm}} = 0.5\ \Delta t_{\text{adv}}$. In this simulation $\Delta t_{\text{adv}} = 0.9\ \Delta t_{\max}$.

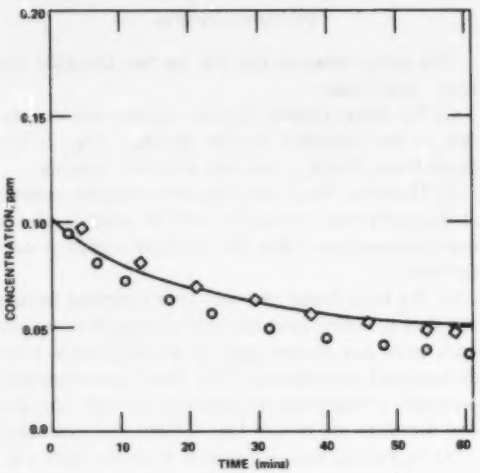

Fig. 4. Solid line is the Gear solution of the A component, the circles are the modified explicit solutions, the diamonds are the implicit solutions for $\Delta t_{chm} = 0.5\ \Delta t_{adv} = 0.5\ \Delta t_{max}$.

over predicts and then decreases faster than the modified explicit.

The results for the B and C components are shown in Figs. 5 and 6, and show that the explicit scheme is much superior to the implicit scheme, since the latter does not even follow the trend of the Gear results for the B component.

Figures 7 and 8 show the explicit and implicit results for the C and D components for the low diffusion case. The high diffusion case is not shown for these components since they have the same character as those shown in Fig. 6.

The chemical reaction for the non-linear system (7)–(9) and the initial conditions imply that the total $A + B + D = 3.3$. Since van Leer's scheme for advection is conservative any deviation of this sum must

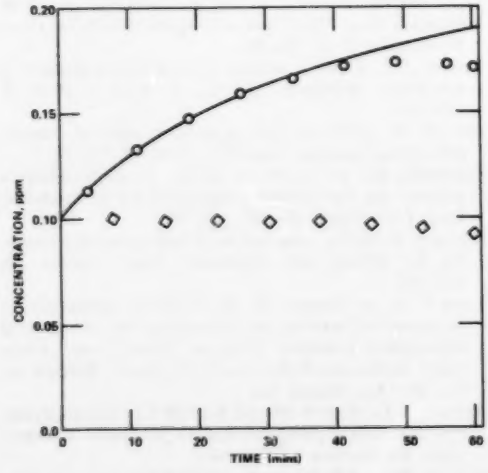

Fig. 5. Same as Fig. 4 except for the B component and $\Delta t_{adv} = \Delta t_{max}$.

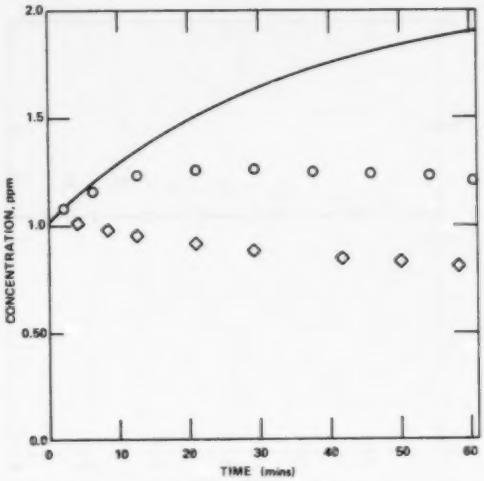

Fig. 6. Same as Fig. 4 except for the B component.

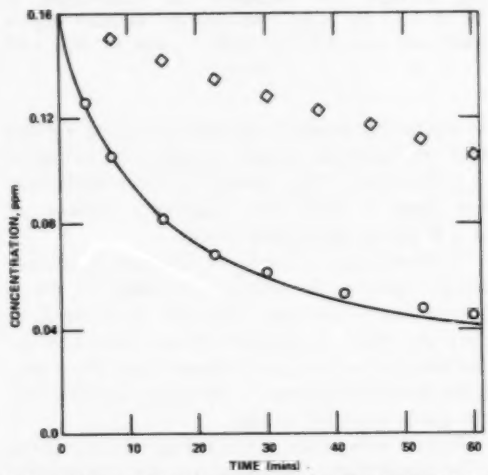

Fig. 7. Same as Fig. 4 except for the C component and $\Delta t_{adv} = 0.9\ \Delta t_{max}$.

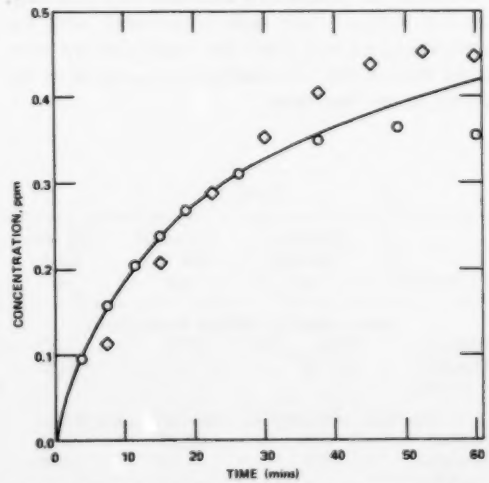

Fig. 8. Same as Fig. 4 except for the D component and $\Delta t_{adv} = 0.9\ \Delta t_{max}$.

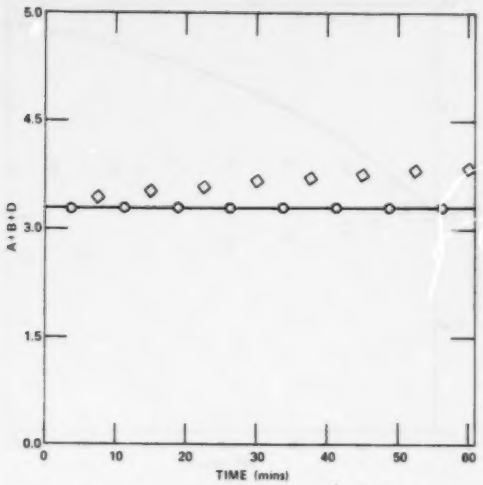

Fig. 9. Solid line represents the conservation of $A + B + D$, the circle represents the modified explicit results and diamonds, the implicit results for $\Delta t_{adv} = 0.9\ \Delta t_{max}$.

be due to the chemical calculations. Figure 9 shows that the modified explicit scheme has conserved $A + B + C$ to within machine accuracy while there has been a small, but significant increase in $A + B + D$ in the implicit scheme.

While accuracy is, of course, important for the numerical scheme, the amount of computer time a scheme uses is also very important. In Table 2, we show the results of various computer simulations for the linear and non-linear chemistry cases. No importance should be attached to the actual numbers, only the trends are worth noting.

Table 2 shows that as expected the implicit scheme is the fastest method. It also shows that the modified explicit is competitive with the implicit.

Some of the experiments discussed here have been done in two and three spatial dimensions using the method of fractional steps. The results are not presented because they are identical in character to the results in one dimension.

Table 2.

Scheme	Advection time step (s)	Chemical time step (s)	CPU time used (s)
Linear chemistry (60 min simulation)			
Implicit	$0.9\Delta t_{max}$(225)	225	14.62
Modified explicit	225	2.39	26.29
Non-linear chemistry (61.7 min simulation time)			
Implicit	225	112.5	3.718
Modified explicit	225	2.39	11.890
Explicit	2.39	2.39	4 min 16.8

IV. CONCLUSIONS

This study indicates that for the two chemical systems studies that:

(1) For linear systems implicit schemes are as accurate as the modified explicit schemes (Fig. 2) and much faster (Table 2) and are therefore superior.

(2) However, this is not true for nonlinear systems as shown by Figs. 3–9 and in fact, the implicit scheme is not conservative while the modified explicit is conservative.

(3) We have found that van Leer's method (results not shown) suffers from the shortcoming that the velocity must not change signs in any dimension (one-dimensional convergence). For many meteorological problems convergence is expected on any one axis and therefore use of van Leer's method is restricted.

(4) Numerical techniques used to solve linear conservation equations (linear chemistry) could handle negative concentration values of the pollutants without becoming unstable, but this was not true when the conservation equations are nonlinear (nonlinear chemistry).

In this paper, we have looked at only two sets of chemical kinetics and two ways of solving those equations. From this limited set of results, one can not say that implicit techniques will not work for all nonlinear chemical systems, the correct interpretation of this paper is that one must proceed with care with nonlinear systems in using implicit methods.

REFERENCES

Aberty R. A. and Miller W. G. (1957) Integrated rate equation for isotopic exchange in simple reversible reactions. *J. chem. Phys.* **26**, 1231–1237.

Bryan K. (1966) A scheme for numerical integration of the equations of motion on an irregular grid free of nonlinear instability. *Mon. Weath. Rev.* **94**, 39–40.

Eskridge R. E. and Demerjian K. L. (1976) Evaluation of a numerical scheme for solving a conservation of species equation. *Proc. 1976 Summer Computer Simulation Conf.*, Washington, D.C., 394–398.

Fromm J. E. (1968) A method for reducing dispersion in convective difference schemes. *J. comput. Phys.* **3**, 176–189.

Gear C. W. (1971) The automatic integration of ordinary differential equations. *Commun. ACM* **14**, 176–185.

Grammeltvedt A. (1969) A survey of finite-difference schemes for the primitive equations for a barotropic fluid. *Mon. Weath. Rev.* **97**, 384–404.

Gupta G. K. (1976) Some new high-order multistep formulae for solving stiff equations. *Math. Comput.* **30**, 417–432.

Long P. E. and Pepper D. W. (1976) A comparison of six numerical schemes for calculating the advection of atmospheric pollution. *Preprints, Third Symp. Atmospheric Turbulence, Diffusion and Air Quality*, Raleigh, pp. 181–187. Am. Meteor Soc.

Reynold S. D., Roth P. M. and Seinfeld J. (1973) Mathematical modeling of photochemical air pollution—I. *Atmospheric Environment* **7**, 1033–1061.

Rizzi A. W. and Bailey H. E. (1976) Split space-marching finite-volume method for chemically reacting supersonic flow. *AIAA J.* **14**, 621–628.

Roache P. J. (1972) *Computational Fluid Dynamics*. 434 pp. Hermosa, Albuquerque.

Roberts K. V. and Weiss N. O. (1966) Convective difference schemes. *Math. Comput.* **20**, 272–299.

Seinfeld J. H., Lapidus L. and Hwang M. (1970) Review of numerical integration techniques for stiff ordinary differential equations. *Ind. Engng Chem. Fundam.* **9**, 266–275.

van Leer B. (1974) Towards the ultimate conservation difference scheme. II. Monotonicity and conservation combined in a scheme. *J. comput. Phys.* **14**, 361–370.

Yanenko N. N. (1971) *The Method of Fractional Steps*. Translated by M. Holt. 160 pp. Springer-Verlag, Berlin.